Rheology 'Slurry preparation'

Additional Information to Cement Course Lection "Slurry preparation"

1. INTRODUCTION

Several aspects to describe the slurry properties are known, some of them are mentioned below:

♦ Flow behaviour

♦ Granulometry

♦ Grindability

♦ Chemistry

♦ . Pumpability

♦ Slump

In this paper the aspects of rheology are considered. Rheology describes the deformation of a body under the influence of stresses.

Ideal solids deform elastically. The energy of deformation is fully recovered when the stresses are removed.

Ideal fluids deform irreversibly - they flow. The energy of deformation is dissipated into the fluids in the form of heat, and it cannot be recovered just by releasing stresses.

Real bodies are neither ideal solids nor ideal fluids.

Only a few liquids of technical or practical importance come in their behaviour close to ideal liquids. The majority of liquids show rheologically a behaviour that classifies them to a region between the liquids and the solids: they are in varying extents both elastic and viscous and may therefore be named "viscoelastic".

1.1 Ideal solids

Ideal Solids subjected to shear stresses react with strain.

① Solid body
unstrained
and deformed
(broken lines)

② Base plate
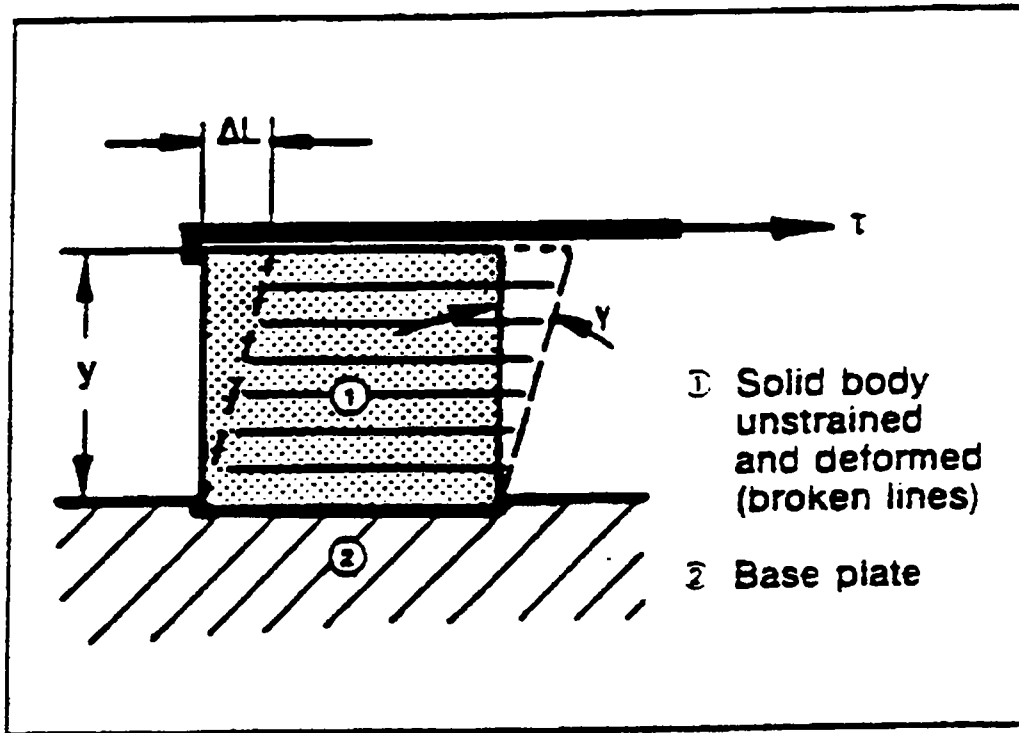
$$\tau \; = \; G \cdot \frac{dL}{dy} \; = \; G \cdot \tan \gamma \; \approx \; G \cdot \gamma$$

τ ■ shear stress ■ force / area

G ■ Young modulus ■ correlation factor

γ ■ strain

y ■ height of the solid body

ΔL ■ deformation of the body as a result of shear stress

The Young's modulus in this equation is a correlating factor linked mainly to the chemical-physical nature of the solid involved. It defines the resistance of the solid against deformation.

1.2 Liquids

The resistance of a fluid against any irreversible positional change of its volume elements is called viscosity. To maintain flow in a fluid, energy must be added continuously.

Viscometry deals specifically with the measurement of the flow behaviour of liquids including those showing a viscoelastic behaviour.
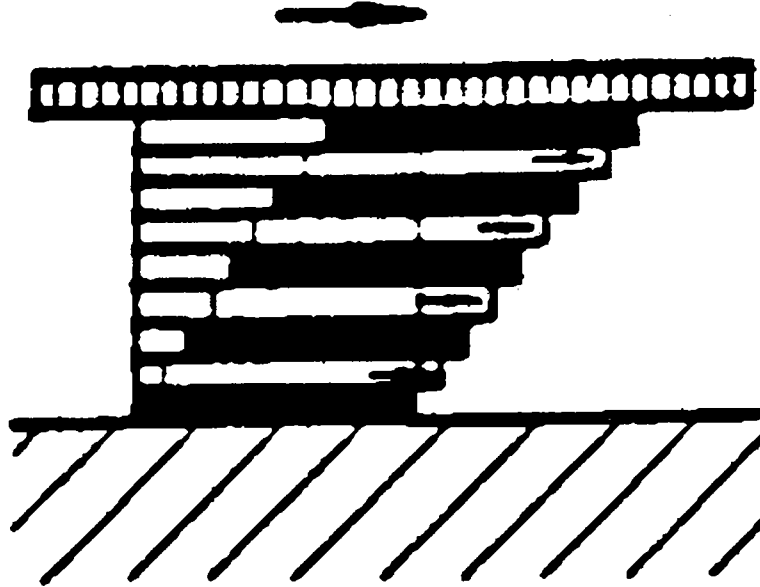
1.2.1   Flow Models

Shear induced flow in liquids can occur in 4 model cases:

1.2.1.1   Flow between two parallel flat plates

One plate moves and the other is stationary.

Flow between two parallel flat plates

1.2.1.2   Flow in the annular gap between two concentric cylinders

One of the two is assumed to be stationary while the other can rotate. This flow can be understood as the displacement of concentric layers sitting inside of each other. A Flow of this type is realised in rotational viscometers with coaxial cylinder sensor systems.
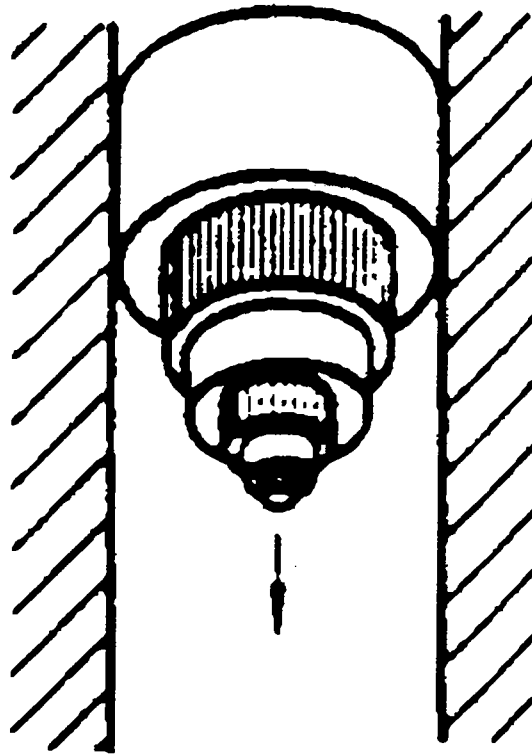
Flow in the annular gap between two concentric cylinders
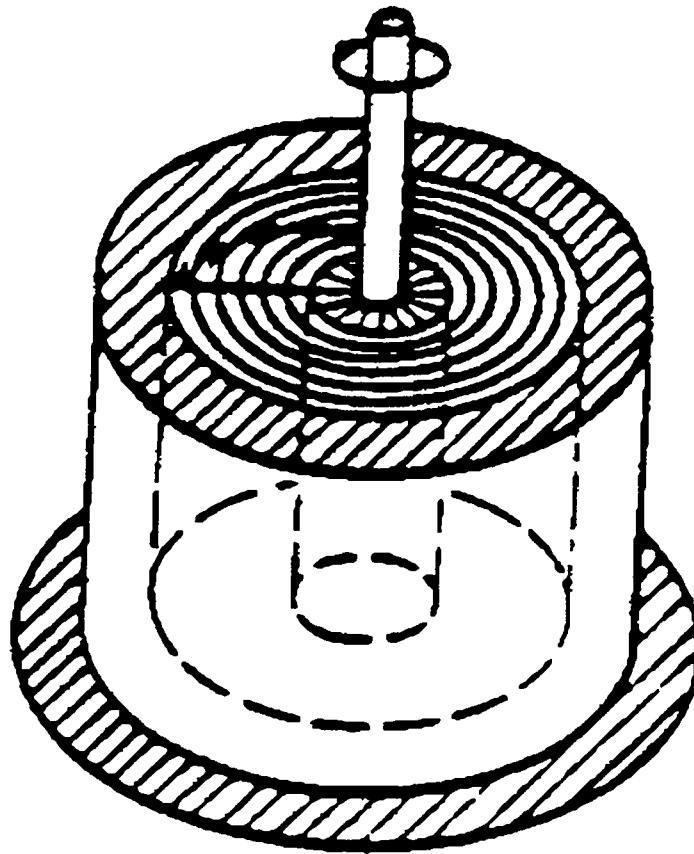
1.2.1.3 Flow through pipes

A difference of pressure between their in and outlets forces the liquid to flow with a parabolic flow speed distribution across the diameter. This resembles a telescopic displacement of tube-like liquid layers sliding over each other.

Flow through pipes

1.2.1.4 Flow between tow parallel plates or between a come and a plate

When one of the two is stationary and the other rotates. This model resembles twisting a roll of coins causing coins to be displaced by a small angle with respect to adjacent coins. This type of flow is realised in rotational viscometers with plate/plate or cone/Plate sensor systems.

Flow between two parallel plates or between a come and a plate
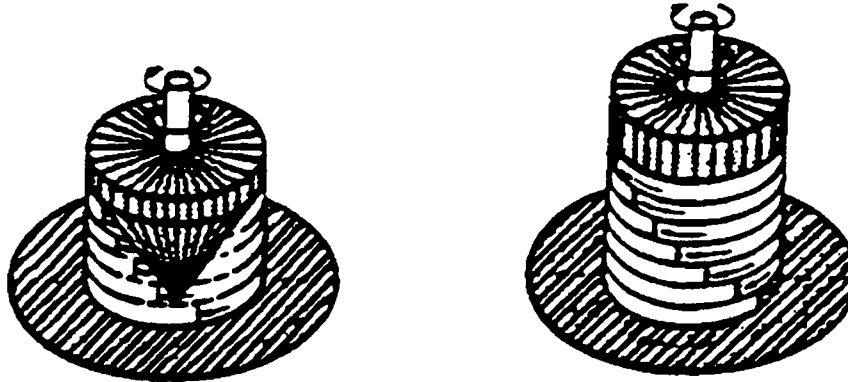
## 2. LAW OF VISCOSITY

To measure the viscosity of liquids requires first the definition of the parameters which are involved in the flow. Then one has to find suitable test conditions which allow the measurement of flow properties objectively and reproducibly.

Isaac Newton was the first to find the basic law of viscometry describing the flow behaviour of an ideal liquid:

$$\tau = \eta \times D$$

The parallel plate model helps to define both shear stress and shear rate:

Small shear rate v_{max} High shear rate
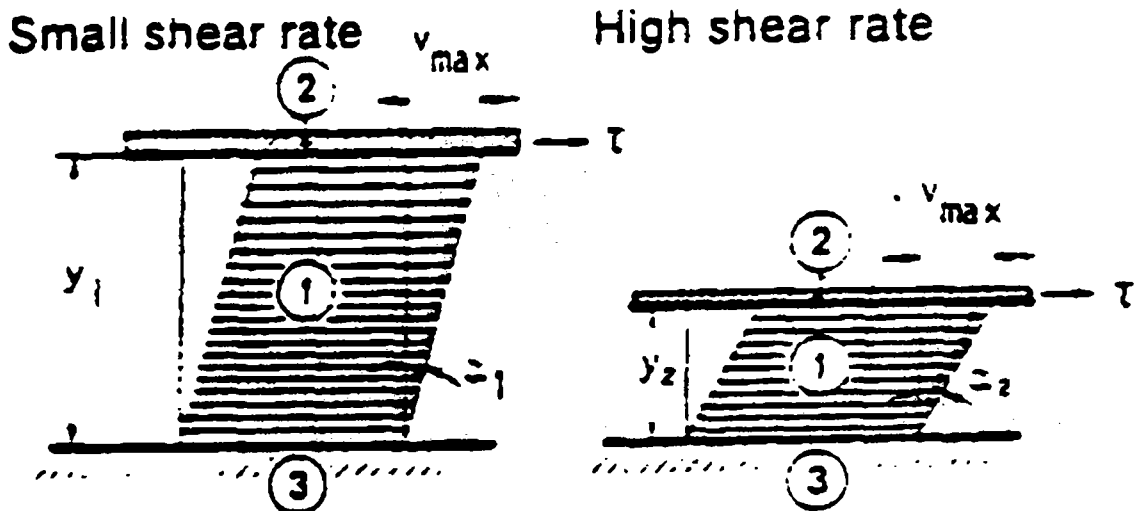
I Liquid sheared

2 Moving plate with surface area A
   to contact the liquid below

3 Stationary plate

2.1   Shear stress

A force F applied to an area A being the interface between the upper plate and the liquid underneath leads to a flow in the liquid layer. The velocity of flow that can be maintained for a given force will be controlled by the internal resistance of the liquid, i.e. by its viscosity.

$$\tau = \frac{F\,(force)}{A\,(area)} = \frac{N}{m^2} Pa\,(Pascal)$$

2.2   Shear rate

The shear stress τ causes the liquid to flow in a special pattern. A maximum flow speed V_{max}. will be found at the upper boundary.

The speed drops across the gap size y down to $V_{min} = 0$ at the lower boundary contacting the stationary plate. Laminar flow means that infinitesimally thin liquid layers slide on top of each other, similar to cards in a deck-of-cards. One laminar layer is then displaced with respect to the adjacent ones by a fraction of the total displacement encountered in the liquid between both plates.

In its general form the shear rate D is defined by a differential:

$$D = \frac{dv}{dx}$$

$$D = \frac{m/s}{m} = \frac{1}{s} [s^{-1}]$$

In case of a linear speed drop across the gap the differential in the equation above can be approximated by

$$D = \frac{V_{max}}{y} [S^{-1}]$$

2.3   Dynamic viscosity

Solving above equation for the dynamic viscosity η gives:

$$\eta = \frac{\tau}{D}$$

$$\eta = \frac{N}{m^2} \times s = [Pa \times s]$$

The unit of dynamic viscosity η is the "Pascal-second" [PA x s]. Often used is also the unit "milli Pascal x second" [mPa x s].

1 Pa x s = 1000 mPa x s

It is worthwhile noting that the previously widely used units of "cementPoise" (cP) of the dynamic viscosity η are interchangeable with the (mPa x s).

1 mPa x s = 1 cP

Typical viscosity values at 20° C:

Substance	mPa x s
petrol	0,65
water	1,0
mercury	1,5
blood (at 27°C)	4 - 15
honey	$\approx 10^4$
bitumen	$\approx 10^8$

2.4   Kinematic viscosity

When Newtonian liquids are tested by means of capillary viscometers, viscosity is determined in units of kinematic viscosity v. The force of gravity is acting as the force driving the liquid sample through the capillary. The density of the sample is one other additional parameter.

Kinematic viscosity v and dynamic viscosity η are linked:

$$v = \frac{\eta}{\delta}$$

v = Kinematic viscosity given in the units of $\dfrac{mm^2}{s}$

Former units of kinematic viscosity were:

"Stokes" [St] or "centi Stokes" [cSt].

1 St = 100 cSt.

$1\dfrac{mm^2}{s} = 1cSt$

δ = density (kg/m^3)

3.   FLOW AND VISCOSITY CURVES

3.1   Viscosity parameters

Viscosity describing the physical property of a liquid to resist shear induced flow may depend on up to 5 independent parameters:

$\boxed{\eta = f\,(S,\,T,\,P,\,D,\,t)}$

(S) This parameter denotes the physical-chemical nature of a substance being the primary influence on viscosity, i.e. whether the liquid is water, oil, honey, etc.

(T) This parameter is linked to the temperature of the substance. Viscosity is heavily influenced by changes of temperature. As an example: The viscosity of mineral oils drops typically by 10% for a temperature increase of only 1°C.

(P) This parameter "Pressure" is not experienced as often as the previous ones. Pressure compresses fluids and thus increased intermolecular resistance. Liquids are compressible under the influence of very high pressures - similar to gases but very much less. Increases of pressure tend to increase the viscosity.

(D) Parameter "shear rate D" is a decisive factor influencing the viscosity of very many liquids. Increasing shear rates may decrease or increase the viscosity.

(t) Parameter "time" denotes the phenomenon that the viscosity of some substances, usually dispersions, depends on the previous shear history, i.e. on the length of time the substance was subjected to continuous shear or was allowed to rest before being tested.

3.2   Flow Curve

The correlation between shear stress and shear rate defining the flow behaviour of a liquid is graphically displayed in a diagram of τ on the ordinate and D on the abscissa. This diagram is called the "Flow Curve".

The most simple type of a flow curve is shown below. The viscosity is assumed to be constant and independent of D.

Simple Flow Curve

$$\eta_1 = \tan\alpha = \frac{\tau_1}{D_1}$$
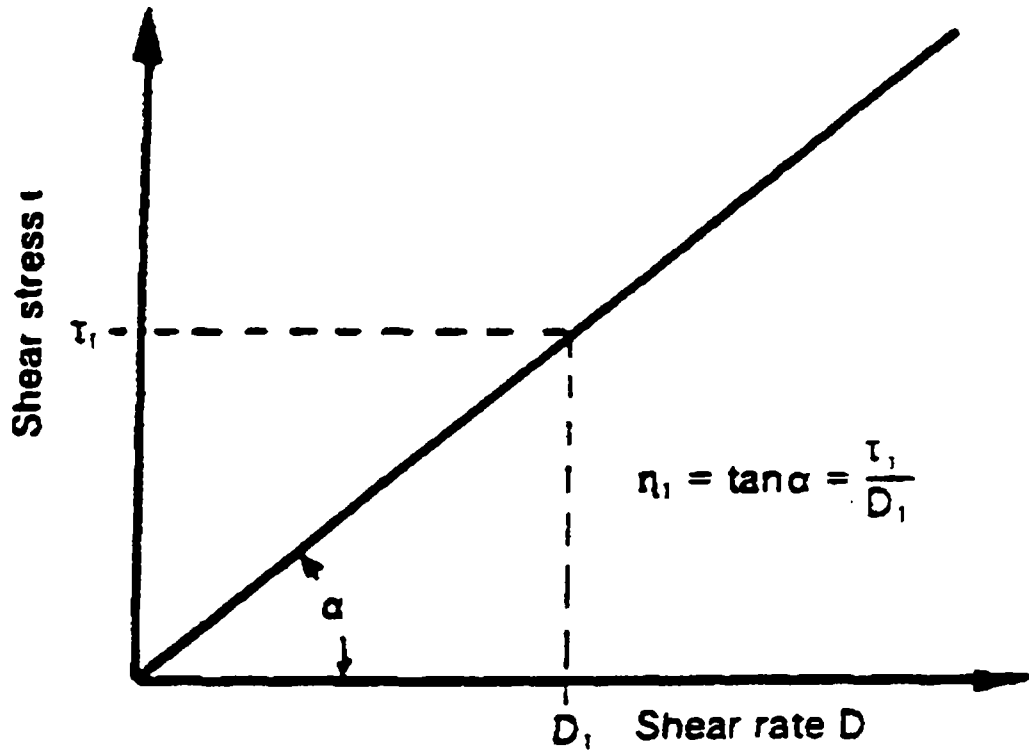
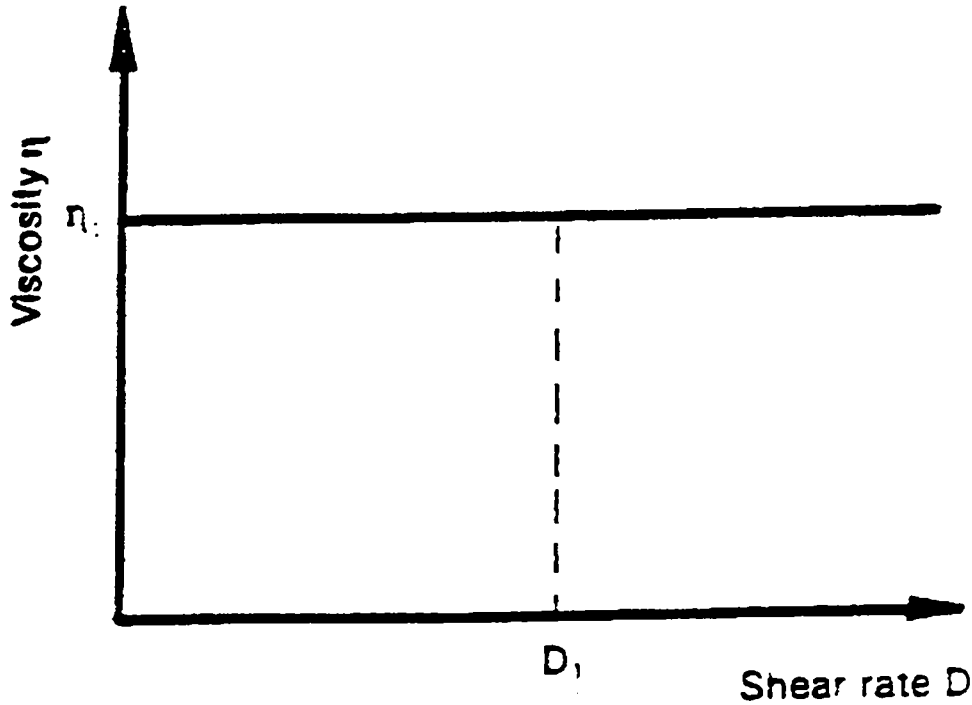### 3.3   Viscosity Curve

Another diagram is very common: η is plotted versus D. This diagram is called the "Viscosity Curve":

Viscosity Curve

Viscosity measurements lead always first to the flow curve. Its results can then be rearranged mathematically to allow plotting the corresponding viscosity curve. The different types of flow curves have their counterparts in types of viscosity curves.

4.   SUBSTANCES

4.1   Newtonian liquids

Newton assumed that the graphical equivalent of his equation for an ideal liquid would be a straight line starting at the origin of the flow curve and would climb with a slope of an angle α. Any point on this line defined pairs of values for τ and D. Dividing one by the other gives a value of η. This value can also be defined as the tangent of the angle α.

Because the flow curve for an ideal liquid is straight, the ratio of all pairs of τ and D-values belonging to this line is a constant. This means, that η is not effected by changes of shear rate. All liquids for which this statement is true are called "Newtonian".
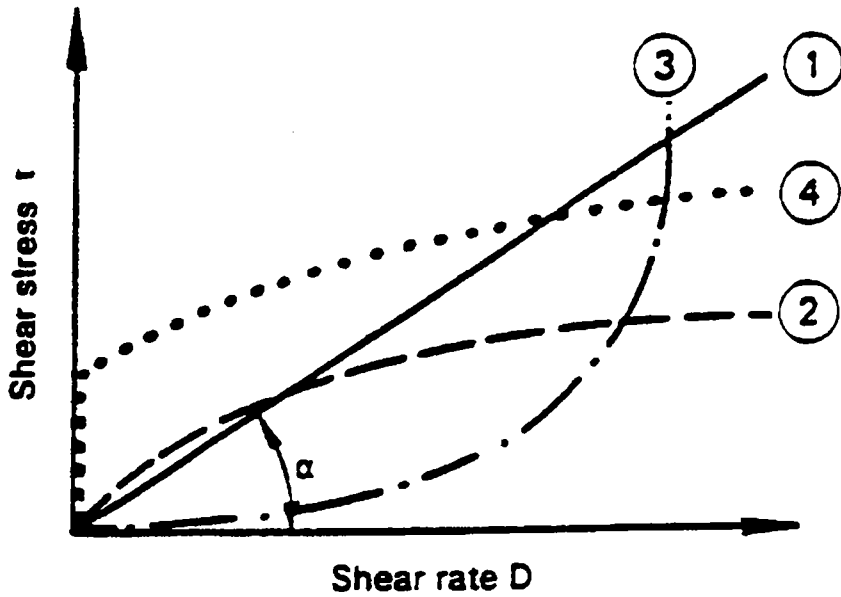
Examples: water, mineral oils, bitumen, molasses, etc.

4.2   Non-Newtonian liquids

All other liquids not showing this simple "ideal" flow behaviour are called "non-Newtonian". They outnumber the ideal liquids by far.

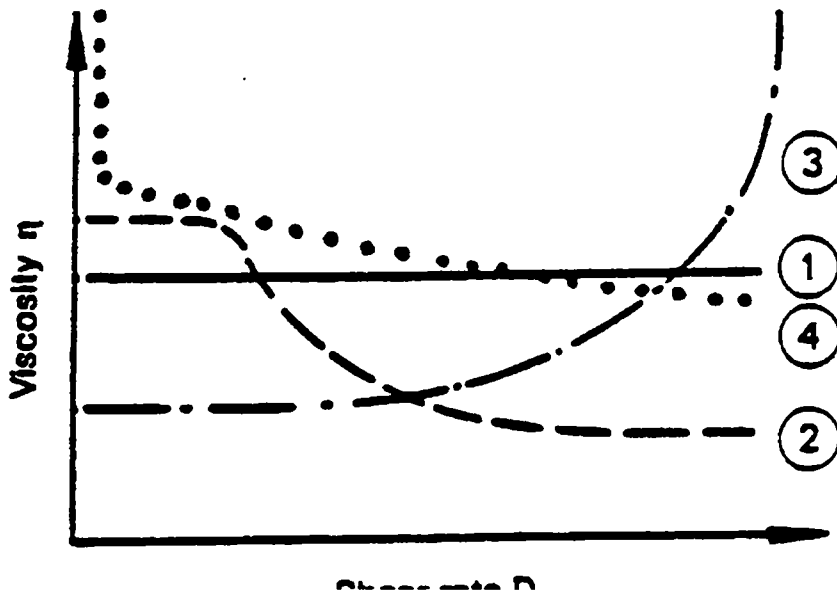## Flow and Viscosity Curves for non-newtonian liquids

Flow curves

Shear rate D

① Newtonian liquid
Non-Newtonian liquids:
② Pseudoplastic liquid
③ Dilatant liquid
④ Pseudoplastic liquid with
  yield point = plastic liquid

Viscosity curves

4.2.1 Pseudoasticity

Very many liquids show drastic viscosity decreases when the shear rates are increased from low to high levels.

Technically this can mean that for a given force or pressure more material can be made to flow, or the energy can be reduced to sustain a given flow rate. Materials which are thinning due to increasing shear rates are called "pseudoplastic". Very many substances such as emulsions, suspensions, or dispersions belong to this group.

4.2.1.1 Mechanism Leading to Pseudoplasticity

4.2.1.1.1 Entropy effect

Many liquid products that seem homogeneous throughout are in fact composed of several ingredients: particles of irregular shape or droplets of one liquid are dispersed in another liquid. On the other hand there are polymer solutions with long entangled and looping molecular chains. At rest all of these materials will maintain an irregular internal order and correspondingly a sizable internal resistance against flow, i.e. a high viscosity.

With increasing shear rates matchstick like particles suspended in the liquid will be turned lengthwise into the direction of the flow. Chaintype molecules in a melt or in a solution can disentangle, stretch, and orient parallel to the driving force. Particle or molecular alignments allow particles and molecules to slip past each other more easily and this shows up as reduces viscosity.

4.2.1.1.2 Disintegration

Shear can also induce irregular lumps of aggregated primary filler particles to break up and this also helps a material with such a filler to flow faster at a given shear stress.

4.2.1.1.3 Reversibility

For most liquid materials the shear thinning effect is reversible - often with some time lag - i.e. the liquids regain their original high viscosity when the shearing is slowed down or is even terminated: the chain-type molecules return to their natural state of non-orientation, deformed droplets return to ball-shape and the aggregates reform due to the Brownian motion.
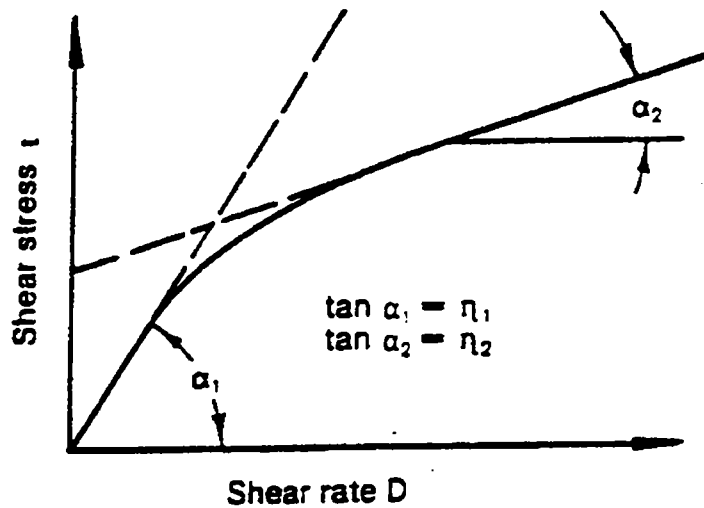
Reversibility of shear thinning effect

- **Liquids at rest**

Liquids flowing

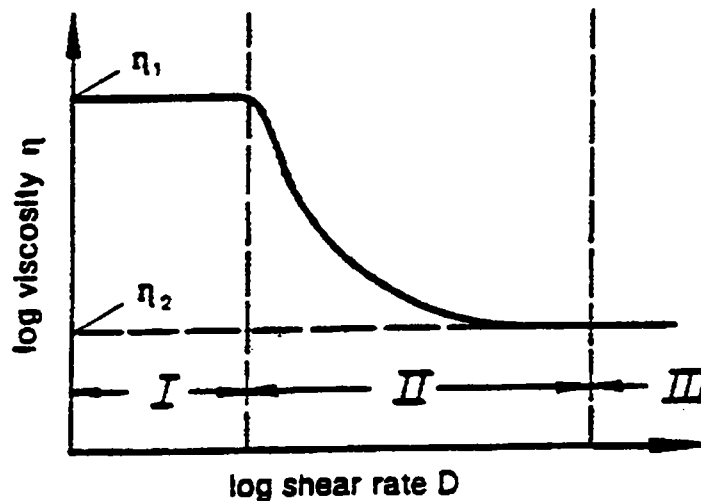| Orientation | Stretching | Deformation | Disaggregation |
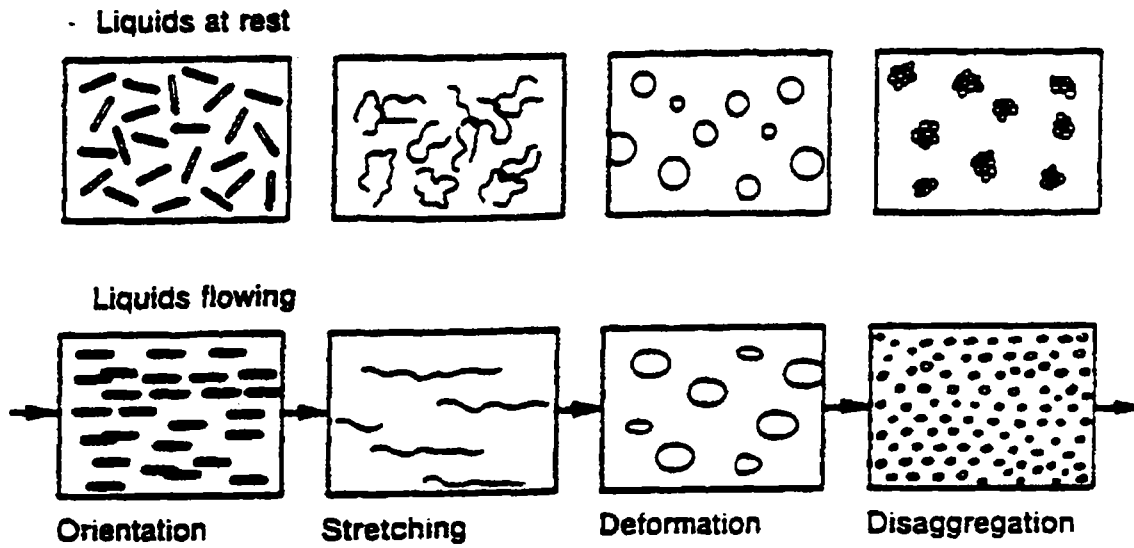
Shear thinning of pseudoplastic liquids is not uniform over the range of very low to very high shear rates:

Non-Uniform Shear thinning of pseudoplastic liquids

Flow curve

$$\tan \alpha_1 = \eta_1$$
$$\tan \alpha_2 = \eta_2$$

Shear rate D

Viscosity curve

log shear rate D

I: First Newtonian range — viscosity η_1 not yet dependent on shear rate.

II: In this range viscosity drops as the result of molecular or particle orientation.

III: Second Newtonian range — viscosity η_2 stays constant independent of further increases of shear rate.

At the low shear rate range the Brownian movement of molecules keeps all molecules or particles at random in spite of initial effects of shear orientation. At very low shear rates pseudoplastic liquids behave similarly to Newtonian liquids having a defined viscosity independent of shear rate. Then follows a shear rate change when the shear rate induced molecular or particle orientation by far exceeds the randomising effect of the Brownian movement: the viscosity drops drastically. Finally the viscosity approaches a finite level. Going to even higher shear rates cannot cause further shear thinning: The optimum of perfect orientation has already been reached. In the low and in the high shear rate ranges - called the first and second Newtonian ranges - the viscosity even of non-Newtonian liquids is more or less independent of shear rate.

4.2.2   Dilatancy

There is one other type of material characterised by a shear rate dependent viscosity: "dilatant" substances increase their viscosity whenever shear rates increase.

Dilatant flow behaviour is found for example in highly concentrated suspensions in which solid particles are mixed with liquids such as plasticizers. The particles are densely packed and the amount of plasticizer added is just sufficient to fill the voids between the particles. At rest or at low coating speeds the plasticizer fully lubricates the particles surfaces and thus allows an easy positional change of particles when forces are applied: this suspension behaves as a liquid at low shear rates. At higher shear rates particles will wedge others apart causing a general volume increase of the plastisol. At this stage the plasticizer's share of the total volume decreases. No longer being sufficient to fill all voids and to keep particle surfaces fully lubricated the plastisol becomes more viscous.

Dilatancy in liquids is rare.

4.2.3   Plasticity

It describes pseudoplastic liquids which additionally feature a yield point. Plastic liquids can be classified with good reasoning to belong to both liquids and solids. They are mostly dispersions which at rest can build up an intermolecular/interparticle network of binding forces (polar forces, van der Waals forces, etc.). These forces restrict positional change of volume elements and give the substance a solid character with an infinitely high viscosity. Forces acting from outside, if smaller than those forming the network, will deform the shape of this solid substance elastically. Only when the outside forces become so big that they can overcome the network forces - surpass the threshold shear stress calls "yield point" - does the network collapse. Volume elements can now change positions irreversibly: the solid turns into a flowing liquid.

Typical substances showing yield points: oil well drilling muds, greases, lipstick masses, toothpastes. Plastic liquids have flow curves which intercept the ordinate not at the origin, but the yield point level of τ_0.
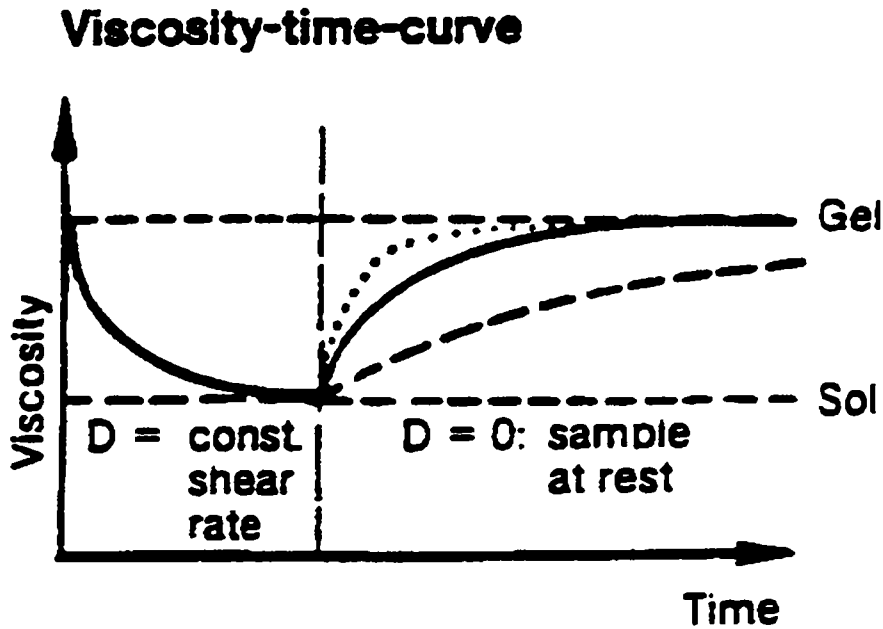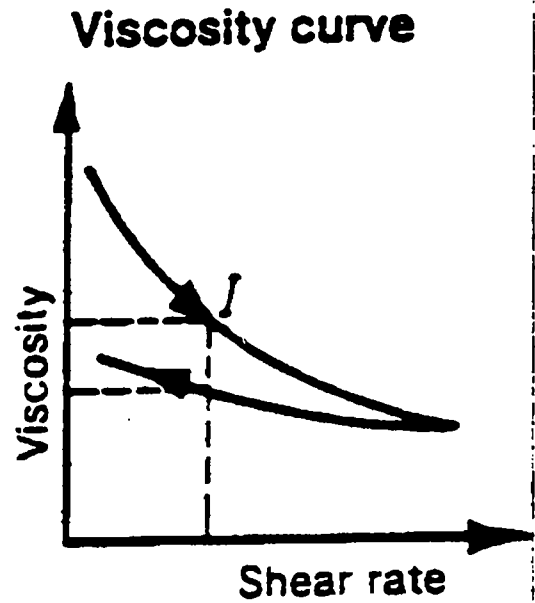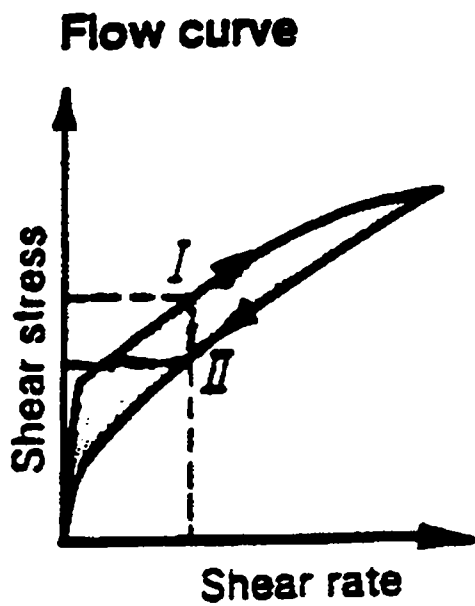
4.2.4   Thixotropy

This term describes a rheological phenomenon of great industrial importance. It calls for some explanations in simplified terms of an otherwise often very complex molecular of particle interaction:

In pseudoplastic liquids thinning under the influence of increasing shear depended mainly on the particle/molecular orientation or alignment in the direction of flow. This orientation will again be lost just as fast as orientation came about in the first place.

Plotting a flow curve with a uniformly increasing shear rate - the "up curve" - one will find that the "down-curve" plotted with uniformly decreasing shear rates will just be superimposed on the "up-curve".

In the flow curve the "up-curve" is no longer directly underneath the "down-curve".

Flow and Viscosity Curves demonstrating Thixotropy

Flow curve

Viscosity curve

Viscosity-time-curve

The hysteresis now encountered between these two curves surrounds an area "A" that defines the magnitude of this property called thixotropy. This area has the dimension of "energy" related to the volume of the sample sheared which indicates that energy is required to break down the thixotropic structure.

4.2.4.1 Mechanism

It is typical for many dispersions that they not only show this potential for orientation but additionally for a particle/molecule-inter-action. This will lead to bonds creating a three-dimensional network structure which is often calls a "gel". In comparison to the forces within particles or molecules, these bonds - they are often hydrogen or ionic bonds - are relatively weak: they rupture easily, when the dispersions is subjected to shear over an extended period of time.

Thixotropy Mechanism
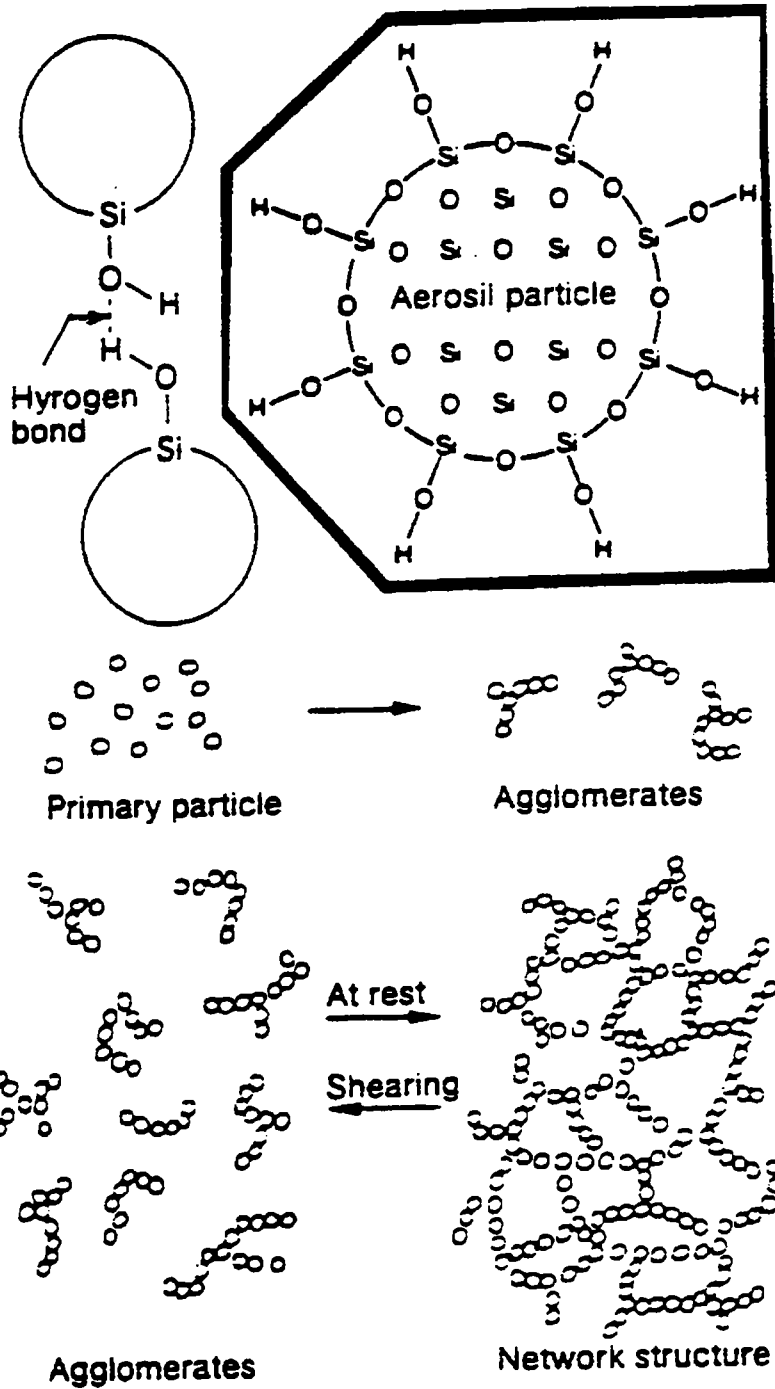
When the network is disrupted the viscosity drops until it asymptotically reaches the lowest possible level for a given constant shear rate. This minimum viscosity level describes the "sol"-status of the dispersion. A thixotropic liquid is defined by its potential to have its structure reformed, when the substance is allowed to rest for an extended period of time. The change of a gel to a sol and of a sol to a gel is reproducible any number of times.

4.3 Rheonexy

Rheopective liquids are characterised by a viscosity increase related to the duration of shear. When these liquids are allowed to rest they will recover the original - i.e. the low - viscosity level. Rheopexy and thixotropy are opposite flow properties.

5.   BOUNDARY CONDITIONS

The mathematical treatment of the physical problem of a fluid being deformed under the influence of forces will lead to very complex differential equations which in their general form cannot be solved. The problem can only lead to an acceptable mathematical solution when test conditions are kept within the framework of these restrictions the Newton's law of viscometry is valid.

The measurement of viscosity requires test conditions providing:

5.1   Laminar flow

The applied shear must lead only to laminar flow. In as much as laminar flow prevents exchange of volume elements between layers samples must be homogeneous to start with. A homogenising effect on heterogeneous samples during testing cannot be expected or permitted.

5.2   Steady state flow

In Newton's law of viscometry the shear stress applied was correlated to shear rate. The shear stress meant was the one that was just sufficient to sustain a constant flow rate. The additional energy required to accelerate or to decelerate the flow cannot be accounted for in the equation.

5.3   No slippage

The shear stress applied must be transmitted from the moving plate across the liquid boundary layer into the liquid. In case that adherence between the moving plate and the liquid is insufficient to transmit the shear stress - the moving plate slips above the non-moving liquid sample - any test results will be meaningless. Problems with slippage often arise with fats and greases.

5.4   Samples must be homogeneous

This requirement means that the sample must react to shear uniformly throughout. If samples are dispersions or suspensions then all ingredients, droplets, or bubbles have to be very small with respect to the thickness of the liquid layer sheared.

In viscometry really homogeneous samples are rare. If dispersions are considered homogeneous because every volume element contains an identical share of all the ingredients, then problems can still occur when the increasing shear encountered during the measurements leads to phase separation, i.e. the dispersion separates into a liquid and a solid layer.

5.5   No chemical or physical changes in the sample during testing

Changes due to processes such as hardening or degradation would be secondary influences on viscosity.

5.6   No elasticity

Samples should be purely viscous. Very many samples such as polymer melts or polymer solutions show a viscous and an elastic response to shear stresses or shear rates. When the latter becomes sizable test results can no longer be evaluated in terms of viscosity.

Comparison between Viscous and Elastic Liquids
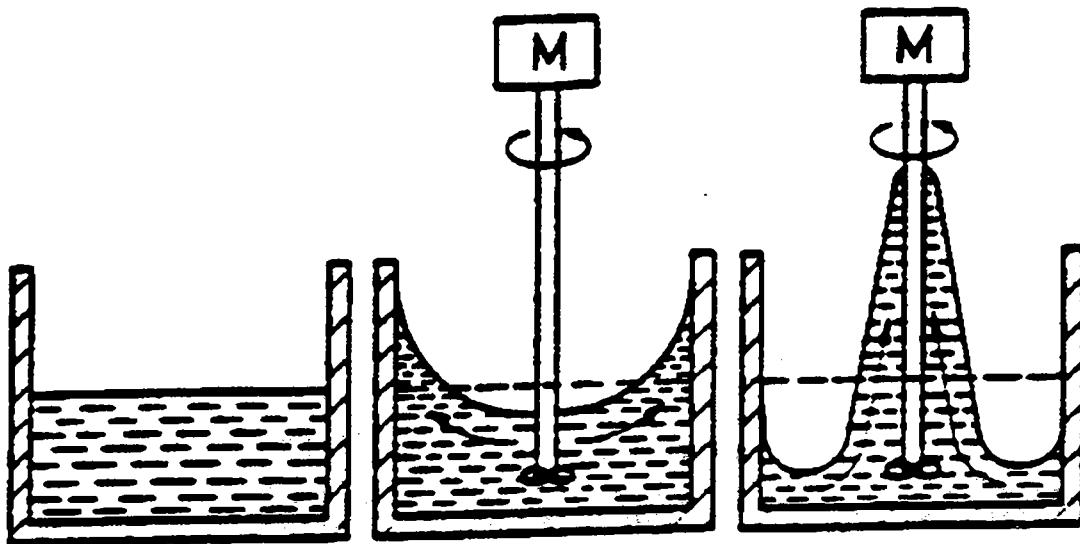
Liquid at rest: rheological phenomena are not apparent.

Viscous liquid: rotating shaft creates centrifugal forces that throw volume elements outwards.

Elastic liquids: rotating shaft creates normal forces exceeding centrifugal forces which means that volume elements are pulled upwards.

In rotational viscometers with coaxial cylinder sensor systems for some samples the elastic response to shear may be so great as to "suck" all the substance out of the annular gap.

Elasticity is a characteristic property of a sample which cannot be subdued by any means. When measuring the viscosity of viscoelastic samples, the maximum of shear rate must be limited to keep the normal stresses from becoming too large so that they ruin the test results.

6. ROTATIONAL VISCOMETERS

6.1 Indication of different models

The principle of rotational viscometers with coaxial cylinder sensor systems and with cone-and-plate sensor systems allows the design of excellent and versatile absolute viscometers. The range of rotational viscometers on the world market varies widely in sophistication and in price. The rheological criteria and boundary conditions mentioned before are being used to grade types of instruments and explain design features and resulting areas of application.

One might imagine that the coaxial cylinder sensor systems for rotational viscometers result from bending both flat plates of the Newton's parallel-plate-model into an inner and outer cyliner. A liquid sample filling the annular gap between the two cylinders can be exposed to shear. Conditions will lead to laminar flow and allow a mathematical treatment of the problem.

6.1.1 Preselect: t look for D

The inner or the outer cylinder is subjected to a defined shear stress or a defined torque while the other cylinder is held at rest. One can now measure the rate of rotation or shear rate resulting.

6.1.2 Preselect D: look for t

The inner or the outer cylinder rotates at a defined rotational speed while the other cylinder is held at rest. One can now measure the resulting shear stress or torque. This is the most common design for rotational viscometers. This type of viscometers can come in two versions:

6.1.2.1 Searle system

The inner cylinder - often called the "rotor" - rotates at a defined speed. The outer cylinder - often called the "cup" - is held at rest. The rotating inner cylinder forces the liquid in the annular gap to flow. The resistance of the liquid being sheared between the stationary and rotating boundaries results in a viscosity related torque working on the inner cylinder which counteracts the torque provided by the drive motor. A torque sensing element - normally a spring that twists as the result of the torque -. is placed between the drive motor and the shaft of the inner cylinder. The twist of the torque spring is a direct measure of the viscosity of the sample tested.

Most viscometer models made world-wide are Searle types. One reason for this tendency is that the good temperature control required for viscosity measurements is more easily accomplished when the outer cylinder does not rotate. Searle type viscometers are limited when low viscous samples have to be tested at high rotor speed. Centrifugal forces affecting the liquid can turn laminar flow to non-laminar flow and eventually to a fully developed turbulence.

Searle Viscometers
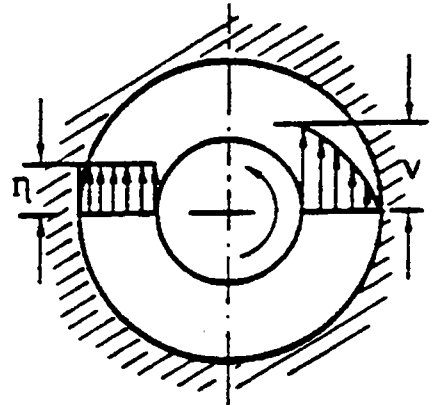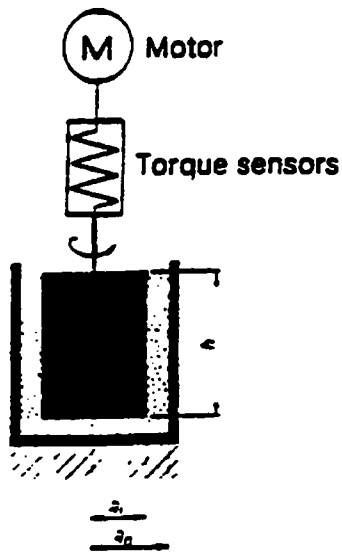
6.1.2.2 Couette system

The outer cylinder rotates at a defined speed. It forces the liquid sample in the annular gap to flow. The resistance of the liquid against being sheared transmits a viscosity related torque onto the inner cylinder, which would induce it also to rotate. This torque is measured by determining just what counteracting torque is required to hold the inner cylinder at stand still. Couette type viscometers are more stable with respect to centrifugal forces.

Couette Viscometers